

# Effects of Anion, pH, and Temperature on Dissolution Behavior of Aluminum Oxide Films

Hochun Lee and Hugh S. Isaacs

Brookhaven National Laboratory, Department of Energy  
Science and Technology, Upton, New York 11973, USA

The dissolution behavior of Al oxide films has been investigated extensively in acidic solutions where porous oxide film is formed<sup>1-3</sup> and in alkaline solutions in the development of Al-air battery.<sup>4,5</sup> The solubility of Al oxides on solution pH is markedly increased in both alkaline and acidic conditions.<sup>6</sup> However, little information is available on the dissolution process in the near neutral solutions. This is due to the difficulty and reliability in measuring the low rate of dissolution in the intermediate pH range.

The main objective in this study is to examine the dependence of dissolution behavior of Al oxides on the type of electrolytic anion (borate, chromate, phosphate, and sulfate), solution pH (pH 3~10), and solution temperature (0~50 °C). It is hoped that this study will lead to a better understanding of pitting corrosion by aggressive anions, because the initiation of the localized corrosion has been attributed to film thinning or the oxide dissolution. For this purpose, cyclic polarization technique has been employed. We found that the simple cyclic polarization measurement offers a very rapid and reliable method to characterize growth and dissolution behavior of Al oxides.

Figure 1 shows the cyclic polarization curve of abraded pure Al in the borate solution. During the first anodic scan, the current increases rapidly and reaches a plateau region. The current keeps decreasing during the subsequent cycles. The polarization behavior in the chromate solution (not shown here) is very similar to that in the borate solution.

Figure 2 shows the polarization curve in the phosphate solution. The current response in the first cycle is similar to that in the borate solution except that the current density at the plateau is somewhat increased. However, the current increases to almost the plateau value at the second anodic scan. The current shows virtually the same potential dependence after the fifth cycle.

Figure 3 shows the result in the sulfate solution. The first cycle shows no plateau. The current is at first lower than that in borate, chromate or phosphate solutions. However, the current continues to rise almost linearly with potential. The current in subsequent cycles continues to decrease until the fourth cycle and then tends to be repetitive, which implies that oxide dissolution is occurring at a certain rate in the dynamic steady state.

The growth of anodic oxide layer on valve metals takes place by a high field conduction mechanism<sup>2,3</sup> given by

$$i = \alpha \exp\left(\beta \frac{E - E_o}{\delta}\right) \quad [1]$$

where the pre-exponential term  $\alpha$  includes concentration of reactant species, vibration frequency of the reactants, and the charge of ion,  $\beta$  = the field constant,  $E$  = the applied potential,  $E_o$  = the potential for zero field in the oxide (flat band potential<sup>7</sup>), and  $\delta$  = the coulomb equivalent thickness. After abrasion the metal rapidly forms an oxide film in air having a thickness  $\delta_o$  prior to immersion. When assuming that a constant oxide dissolution rate  $R$  takes place independent of applied potential,  $\delta$  is expressed by

$$\delta = \delta_o + (\Delta\delta - Rt) / \sigma \quad [2]$$

where  $\sigma$  is the roughness factor and  $\Delta\delta$  is proportional to the anodic charge change.

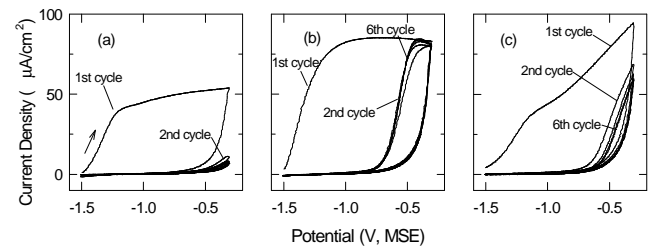
Figure 2 shows the simulated polarization curves based on Eq. [1] and [2]. The simulated curve without oxide dissolution (Fig. 2a) is similar to that observed for the results in the borate (Fig. 1a), while the curve in Fig. 2c with a relatively high oxide dissolution rate (14  $\mu\text{A}/\text{cm}^2$ ) is similar to that observed in the phosphate (Fig. 1b). This demonstrates that the polarization behavior in the borate and the phosphate can be accounted for in terms of a high field conduction model and dissolution of oxide. However, the simulation result does not

account for the behavior in the sulfate solution (Fig.1c) where the current behavior at the first cycle is very different from those in borate and phosphate solutions. This means that polarization behavior in the sulfate does not follow the high field conduction model.

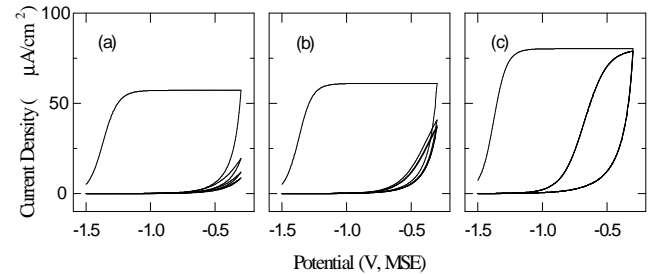
In addition, the polarization behavior in various solution pH and temperature will be compared and the dissolution rate as a function of pH and temperature will be reported.

## References

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**Figure 1.** Polarization characteristics of abraded Al in (a) phosphate (0.25 M NaH<sub>2</sub>PO<sub>4</sub> / 0.25 M NaHPO<sub>4</sub>, pH 6.0), (b) borate (0.42 M H<sub>3</sub>BO<sub>3</sub> / 0.08 M Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>, pH 8.4), and (c) sulfate (0.5 M Na<sub>2</sub>SO<sub>4</sub>, pH 5.8) solution at 5 mV/s.



**Figure 2.** Simulated polarization curves for potential cycles based on high field conduction model. (a) without oxide dissolution, (b) with an equivalent oxide dissolution rate of 4  $\mu\text{A}/\text{cm}^2$  and (c) 14  $\mu\text{A}/\text{cm}^2$ .